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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C01B 3/26, 3/50

A1

(11) International Publication Number: WO 99/43610

(43) International Publication Date: 2 September 1999 (02.09.99)

(21) International Application Number: PCT/US99/03574

(22) International Filing Date: 19 February 1999 (19.02.99)

(30) Priority Data:

60/075,814	24 February 1998 (24.02.98)	US
09/231,862	14 January 1999 (14.01.99)	US

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

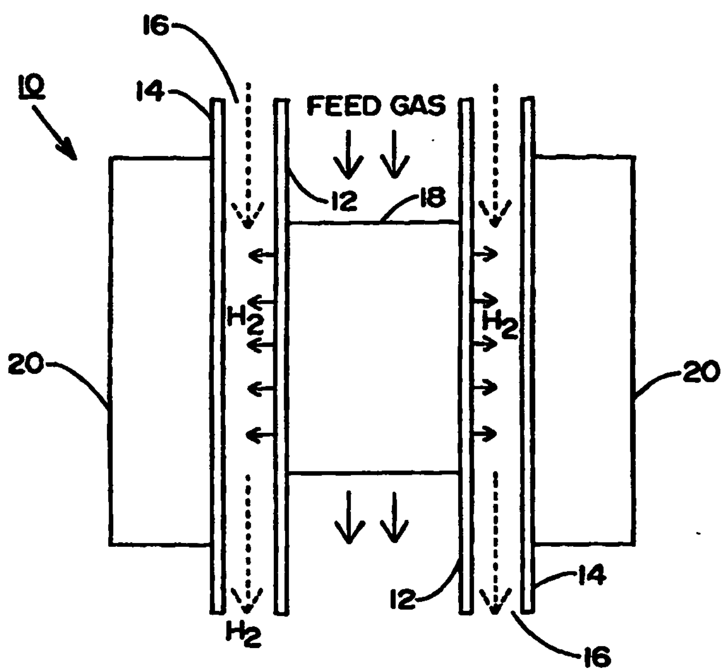
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: USE OF A MEMBRANE REACTOR FOR HYDROGEN PRODUCTION VIA THE DIRECT CRACKING OF HYDROCARBONS

(57) Abstract

A process for producting substantially pure hydrogen by contacting a stream of a hydrocarbon gas with a nickel containing catalyst in a membrane reactor. The membrane reactor combines a hydrogen permeable membrane and a catalyst capable of producing hydrogen via the direct cracking of hydrocarbons. The stream of a hydrocarbon gas is contacted with the catalyst at a temperature in the range of about 400 to 900 °C which results in the conversion of the gas to substantially pure hydrogen, which selectively permeates through the membrane wall.



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USE OF A MEMBRANE REACTOR FOR HYDROGEN PRODUCTION VIA THE DIRECT CRACKING OF HYDROCARBONS

Field of the Invention

This invention relates generally to the production of hydrogen, and more specifically to the use of a membrane reactor for hydrogen production by the direct cracking of a hydrocarbon.

Background of the Invention

Inorganic membranes such as palladium (Pd), palladium-silver (Pd-Ag) and several other alloys have been utilized in the past to separate hydrogen from other reactants and products in various reactions including hydrogenations, and dehydrogenations. Due to the high cost of these membranes, a great effort has been also devoted over the last several years to the development of composite and alloy membranes. Membranes of this type consist of a thin palladium film (providing permselectivity) coated on a porous or non-porous support that provides the required mechanical strength. A special type of membrane has been developed by Buxbaum and co-workers (*J. Membr. Sci., 85, 29 (1993). and U.S. Patent Nos. 5,149,420 and 5,215,729*). This membrane takes advantage of the fact that several refractory metals such as niobium (Nb), tantalum (Ta), zirconium (Zr) and Vanadium (V) are one order of magnitude more permeable to hydrogen than palladium and have acceptable mechanical strength. An electroless plating technique was used to deposit a thin palladium film (1-2 μm thickness) on the surface of the refractory metals. Membranes prepared in this manner, and particularly Pd-Nb and Pd-Ta, ensure high purity of the extracted hydrogen and are capable of permeating higher amounts of hydrogen than pure palladium membranes. In addition, they are stronger and more durable and can be used at higher temperatures.

Applicants have previously demonstrated the ability to produce hydrogen via the direct cracking of methane and other suitable hydrocarbons. The details of this process are described in a separate invention disclosure entitled **Hydrogen Production via the Direct Cracking of Hydrocarbons**. The methane cracking reaction however, is limited by thermodynamic equilibrium. Furthermore, kinetic

experiments suggest that the rate of the reaction is inhibited by the hydrogen product. For both of these purposes, it would be beneficial to remove the hydrogen produced during the reaction from the reaction zone.

Summary of the Invention

In a separate invention disclosure we have demonstrated the feasibility of producing hydrogen via the direct cracking of methane over a Ni-containing catalyst in a conventional fixed bed reactor. The performance of that design however, is affected negatively by the presence of hydrogen in the reaction zone. The above review of the prior art suggests that the utilization of a membrane reactor could improve the performance of the system for the catalytic cracking of methane by effectively removing hydrogen from the reaction zone.

It is therefore an object of the present invention to efficiently produce high purity hydrogen by the catalytic cracking of hydrocarbons.

It is another object of the present invention to provide a method of producing hydrogen by direct cracking of hydrocarbons using a membrane reactor.

It is another object of the present invention to provide a method of producing substantially pure hydrogen without carbon monoxide contamination by the direct cracking of hydrocarbons in a membrane reactor using a nickel containing catalyst.

It is yet a further object of the present invention to provide a method of producing high purity hydrogen by direct cracking of methane at low temperatures using a silica supported nickel containing catalyst in a membrane reactor.

The present invention overcomes the problems described above and demonstrates the feasibility of producing substantially pure hydrogen by the direct cracking of hydrocarbons by the use of a membrane reactor. A membrane reactor can remove hydrogen from the reaction zone, and therefore, eliminate its negative effects on both reaction equilibrium and the reaction rate. As a result, the utilization of a membrane reactor can increase significantly the efficiency of the hydrogen production process. The membrane may be of any type of material that is selectively permeable only to hydrogen, and can thus effectively separate hydrogen from carbon

monoxide and other components of the reacting mixture (e.g., unreacted hydrocarbons, carbon dioxide, water vapor, etc.). The invention has been demonstrated with a Pd-Nb-type of membrane which is believed to have certain advantages as discussed in the background section of this application. This, however, does not in any case exclude the use of other membranes either of the composite or mixed ion ceramic type. In one embodiment, the membrane preferably comprises Pd-Nb. The invention may be applicable to cracking any suitable hydrocarbon such as methane, natural gas, ethane, ethylene, propane, propylene, butane, pentane, hexane or mixtures thereof, and hydrocarbons with molecular weights in the gasoline and diesel range.

The membrane reactor utilizes a catalyst bed which preferably comprises a nickel containing catalyst supported on a silica support. The hydrogen produced in the reactor zone selectively permeates through the membrane wall and is carried away by a sweeping gas. In operation the reactor typically operates at a temperature in the range of about 400 to 900 °C.

Brief Description of the Drawing

For a fuller understanding of the nature and objects of the invention, reference should be made to the following detailed description of a preferred mode of practicing the invention, read in connection with the accompanying drawings, in which:

FIG. 1 is an enlarged side sectional view of the catalyst reaction zone of double tubular catalytic membrane reactor.

FIG. 2 represents a plot of a comparison of methane conversion over 0.2 g of a 16 wt% Ni/SiO_2 catalyst at 550°C in a conventional fixed bed reactor and the reactor of Fig. 1.

FIG. 3 represents a plot of the comparison of methane conversion over 0.2 g of a 16 wt% Ni/SiO_2 catalyst at 7600 h^{-1} in a conventional fixed bed reactor and the reactor of Fig. 1.

FIG. 4 is an enlarged side sectional view of the catalyst reaction zone of an alternative design of a fixed bed catalytic reactor having a membrane separator.

Detailed Description of the Invention

The invention was demonstrated with the double tubular catalytic membrane reactor (10) depicted in Figure 1. The Pd-Nb membrane tube utilized has an outer diameter of 9.525 mm (3/8 in.) and a wall thickness of 0.25 mm; and was prepared according to the procedures described in the corresponding patents (*U.S. 5,149,420 and 5,215,729*) covering its manufacture and use, which are incorporated herein by reference. The reactor consists of an inner membrane tube (12) and an outer stainless steel or quartz tube (14) which define a flow passageway (16). A catalyst bed (18) is located within the inner tube (12). Electrical heater (20) controls the reaction temperature. The hydrogen produced in the reactor zone selectively permeates through the membrane wall and is carried away by a sweeping gas indicated by the dotted arrows. The outer tube (SS, 1 in. OD, 0.028 in. thickness) is directly connected to a sweeping gas supply (not shown). The membrane occupied the central section of the inner tube and was connected to the reactor inlet and outlet with appropriate unions. The catalyst (16 wt% Ni/SiO_2) was packed within the membrane tube and the produced hydrogen was purged with an inert sweeping gas such as argon in the shell side. Additional hydrogen is also exiting the reactor at the bottom of the catalyst bed, as indicated by the solid arrows.

In a typical experiment, 0.2 g of the catalyst (25-35 mesh) were uniformly diluted in 0.3 g of inert silica (25-35 mesh) and subsequently packed into the middle section of the membrane tube. The reactor was flushed with inert gases and it was heated to the reaction temperature. The sweeping argon flow rate was held constant at 150 cc/min. A feed indicated by the top solid arrows consisting of 20% CH_4 in He was introduced in the reactor to start the reaction. Exit streams from both the sweeping and reaction sides were analyzed by gas chromatography.

It should be understood that the current invention is not limited to the specific configuration depicted in Figure 1. In fact, any other configuration that effectively combines a catalyst capable of producing hydrogen via the direct

cracking of hydrocarbons and a membrane that is selectively permeable only to hydrogen can be incorporated in the current invention. The configuration of Fig. 1 was chosen for the demonstration of the invention because of its simplicity. Another example of a membrane reactor configuration suitable for use in the present invention is shown in Fig. 4 wherein a fixed bed catalytic reactor or fuel processor is equipped with a membrane separator. The fuel processor, which employs direct cracking, converts the hydrocarbon feed to hydrogen and carbon products and with the membrane separator, selectively extracts hydrogen to produce an essentially pure hydrogen product. The membrane separator reactor 30 illustrated in Fig. 4 includes a bundle of metal or metal alloy membrane tubes 32, up to fifty or more small hollow tubes sealed at one end 34, and open at the opposite end 36. The tubes are surrounded by a bed of catalyst material 38, and all together contained within the outer shell 40 of the reactor. In operation, the hydrocarbon gas is fed through an inlet port 42 and is cracked in internal chamber 44. The hydrogen formed from the cracking permeates the selectively porous membrane tubes 32 and travels to exit port 48 (see small arrows), while carbon monoxide, other reaction products, and unreacted hydrocarbons exit through port 46.

As can be seen from the above description, the hydrocarbon gas feed enters one end of the reactor, passes through the catalyst bed, and the reaction products and unreacted hydrocarbons exit at the other end. In the membrane separator, the flow of the hydrogen goes from the outside to the inside of the membrane tubes. The flow of essentially pure hydrogen from all the membrane tubes are combined into a common header 50 and collected at exit port 48. Other alternate reactor configurations for this type of reactor in commercial operations may include fluidized bed or moving bed reactors.

The catalyst used in the present invention will eventually deactivate as a result of carbon deposition. The carbon deposited on the catalyst may be recovered and used in electrochemical applications (superconductors, electrodes and fuel cells) or fuel storage applications. Alternatively, the deactivated catalyst can be fully regenerated by oxidization in air or steam gasification of the deposited carbon.

Figure 2 compares the methane conversions obtained from a conventional fixed bed reactor and the reactor of Fig. 1 at 550°C at different space velocities. The CH_4 conversion in the conventional fixed bed reactor ranged from 31.7% at a space velocity of 60000 h^{-1} to 42.2% at 7500 h^{-1}. In the membrane reactor the CH_4 conversion increased from 37.2% at a 60000 h^{-1} to 70.8% at 7500 h^{-1}. The difference (and hence the benefits of the utilization of the membrane reactor) was more significant at low space velocities because the negative effects of hydrogen are more pronounced under these conditions.

The hydrogen permeability of the Pd-Nb membrane utilized in this demonstration was measured at different temperatures and found to increase with temperature. Thus it was hypothesized that the observed conversions of methane may benefit more by the use of the membrane reactor at higher temperatures. This was indeed demonstrated experimentally as shown in Figure 3, for temperatures up to 550°C. At even higher temperatures, the difference in the performance of the two types of reactor was decreased probably due to the deterioration of the membrane under these conditions.

While the present invention has been particularly shown and described with reference to the preferred mode as illustrated in the drawing, it will be understood by one skilled in the art that various changes in detail may be effected therein without departing from the spirit and scope of the invention as defined by the claims.

We Claim:

1. A process for producing substantially pure hydrogen which comprises:

(a) providing a membrane reactor which includes a hydrogen permeable membrane and a catalyst bed; and

(b) contacting a stream of a hydrocarbon with said catalyst at a temperature in the range of about 400 to 900°C which results in the conversion of said gas to substantially pure hydrogen, which selectively permeates through the membrane wall.

2. The process of claim 1 in which the membrane is selectively permeable only to hydrogen, and effectively separates hydrogen from carbon monoxide and other components of the reacting mixture.

3. The process of claim 1 in which said membrane comprises a metal or metal alloy.

4. The process of claim 1 in which said membrane comprises Pd or a Pd alloy.

5. The process of claim 1 in which said membrane comprises Pd-Nb.

6. The process of claim 1 in which the membrane comprises a composite or ceramic type membrane.

7. The process of claim 1 in which the catalyst contains nickel and is supported on a silica support.

8. The process of claim 1 in which the catalyst contains at least 5 wt. % nickel.

9. The process of claim 1 in which the hydrocarbon gas is one selected from the group consisting of methane, natural gas, ethane, ethylene, propane, propylene, butane, pentane, hexane or mixtures thereof, and hydrocarbons with molecular weights in the gasoline and diesel range.

10. The process of claim 1 in which the hydrocarbon gas is mixed with an inert carrier gas.

11. The process of claim 1 in which the catalyst is regenerated by oxidation of the deposited carbon in air.

12. The process of claim 1 in which the catalyst is regenerated by steam gasification of the deposited carbon.

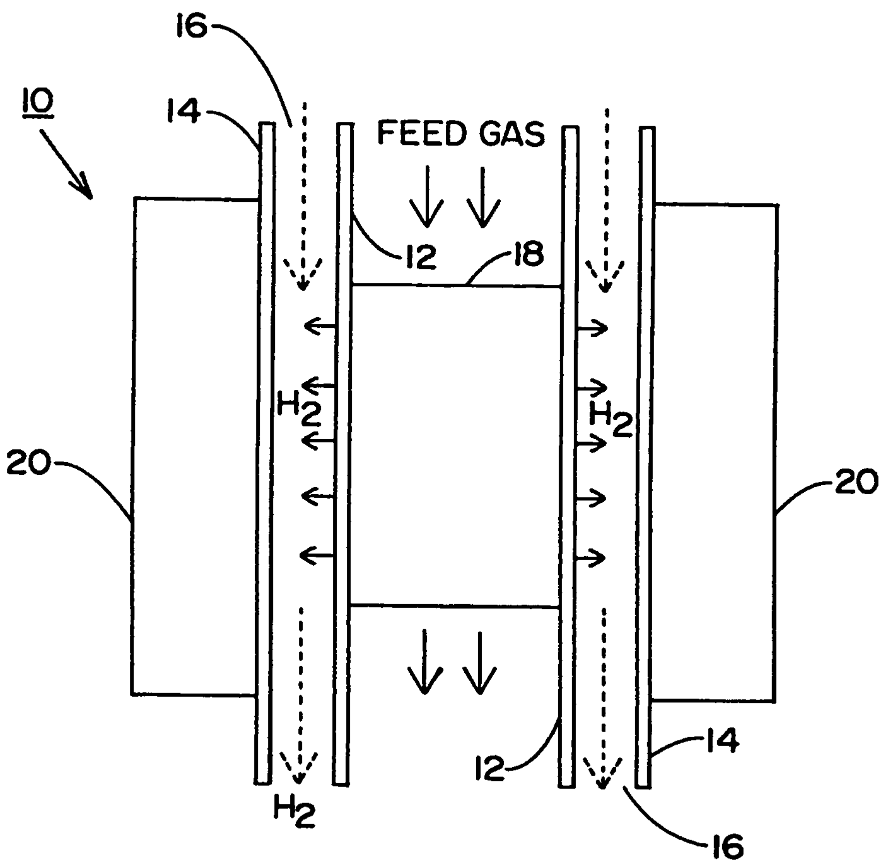
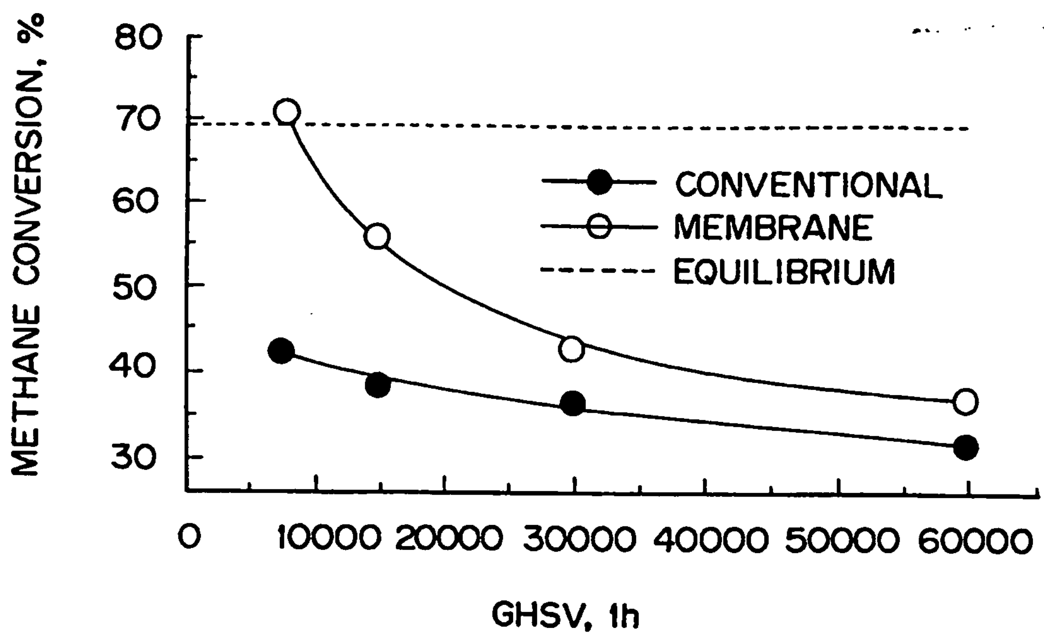


FIG. 1


METHANE CONVERSION, %
80
70
60
50
40
30
CONVENTIONAL
MEMBRANE
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0
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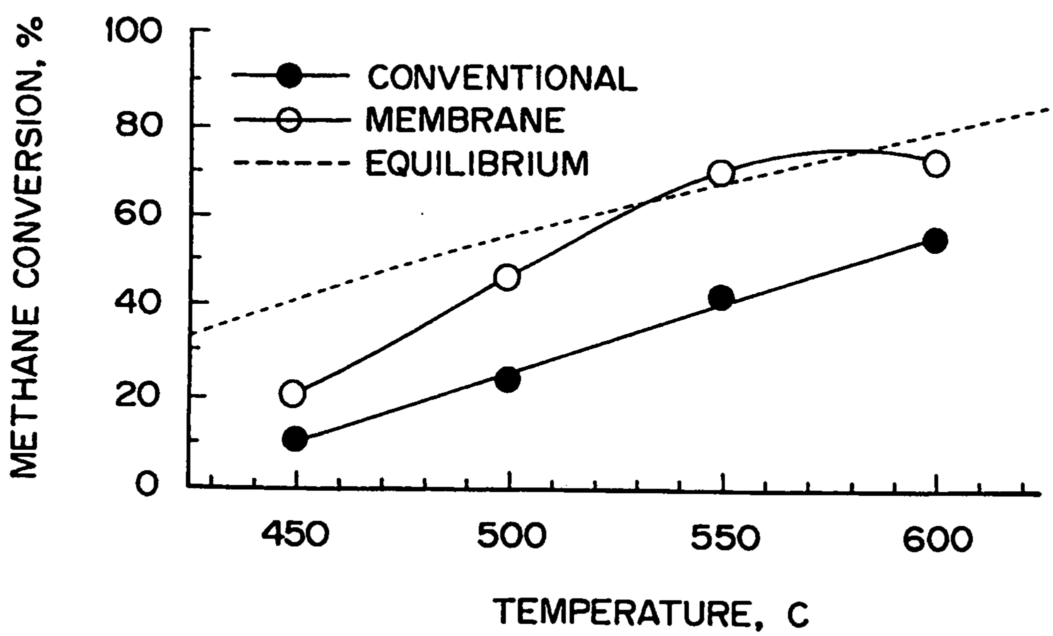
GHSV, 1h

FIG. 2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40
20
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MEMBRANE
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450
500
550
600
TEMPERATURE, C

FIG. 3

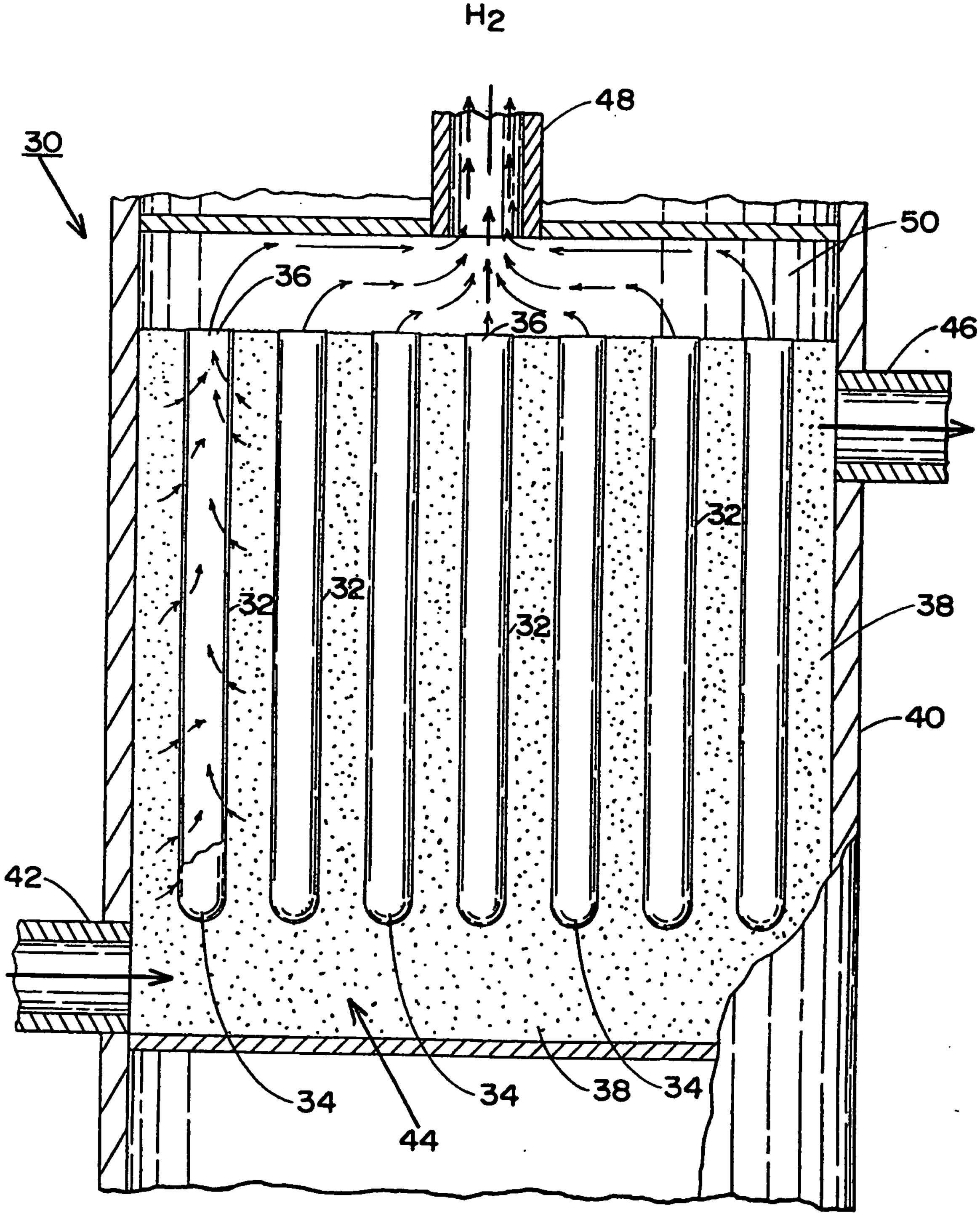

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/03574

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C01B 3/26, C01B 3/50
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01B, C10G, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EDOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4981676 A (RONALD G. MINET ET AL), 1 January 1991 (01.01.91), column 1, line 35 - line 41; column 2, line 5 - line 16; column 3, line 23 - line 55, column 5, line 42 - line 45; claims, abstract	1-3,6-10
Y		11-12
	--	
X	US 5326550 A (ALAA-ELDIN M. ADRIS ET AL), 5 July 1994 (05.07.94), column 4, line 29 - line 38; column 5, line 7 - line 10, abstract	1-6,8
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 June 1999	0 5. 07. 99
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International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

03/05/99

International application No.

PCT/US 99/03574

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